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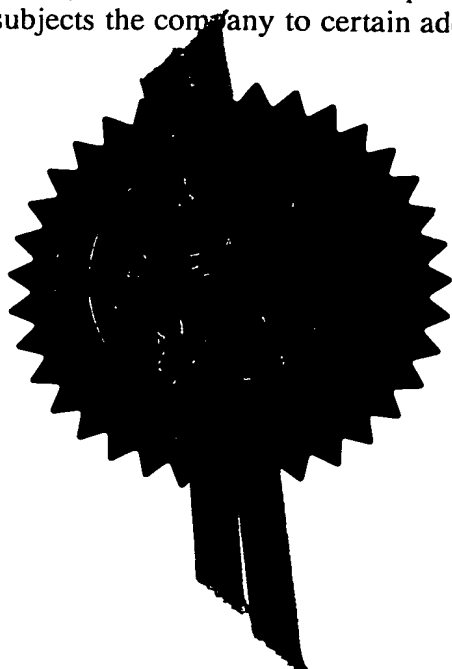
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Signed

Andrew Grey

Dated

22 June 2000

Act 1977

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18JUN99 E455436-1 D02392
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Request for grant of a patent

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The Patent Office

Cardiff Road
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1. Your reference **PB767/GB/RGMS**

2. Patent applic **9914139.2**
(The Patent Office)

18 JUN 1999

3. Full name, address and postcode of the or of each applicant (underline all surnames)
**ALBRIGHT & WILSON UK LIMITED
210-222 HAGLEY ROAD WEST
OLDBURY
WEST MIDLANDS B68 0NN**

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND

4. Title of the invention
LEATHER TANNING

5. Name of your agent (if you have one) **R G M SAVIDGE**
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)
**ALBRIGHT & WILSON UK LIMITED
PATENTS DEPARTMENT
210-222 HAGLEY ROAD WEST
OLDBURY
WEST MIDLANDS B68 0NN**

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of filing (day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing (day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:
a) any applicant named in part 3 is not an inventor, or
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See note (d)) **NO**

PB767/GB

PATENTS ACT 1977

PRELIMINARY SPECIFICATION
(Description)

LEATHER TANNING

Applicant :

ALBRIGHT & WILSON UK LIMITED

Inventors :

LEATHER TANNING

The present invention relates to a novel process for tanning leather.

Tanning is a process for the preservation of skins, by which is meant the collagen-containing integuments of vertebrates including mammals (e.g. cows, pigs, deer, goats, sheep, seals, antelope, mink, stoats and camels), fish, (e.g. sharks), reptiles (e.g. snakes, lizards and crocodiles), and birds (e.g. ostrich). Skins comprise a layer of collagen, and tanning entails reacting the collagen with a cross linking, or tanning, agent to cross link reactive sites within the collagen molecule. The product of the cross linking is leather, which is substantially less susceptible than skin to bacterial degradation.

A consequence of the cross linking is an increase in the minimum temperature at which the wet leather tends to shrink. This shrink temperature is often used as an indication of the degree of tanning.

The collagen layer of the skin is separated from fats, connective tissue and other subcutaneous protein, and optionally from the outer keratinous layer, by a combination of chemical and physical steps. The former may include liming, bating, pickling and/or degreasing.

The skin is then subjected to treatment in one or more stages with various tanning agents selected to give the desired end properties.

The main types of tannage are:- vegetable tannage, based on tannin as the active cross linking agent; mineral tannage using various polyvalent metal salts, especially salts of chromium, aluminium, iron, or zirconium; and synthetic tanning agents, referred to as "syntans". Syntans include replacement syntans which are active tanning agents capable of tanning leather when used as the sole tannage e.g. by reacting with collagen at two or more sites to form cross links, and auxiliary syntans which are added to other tannages to modify the character of the leather but which are not in themselves active tanning agents. Auxiliary syntans are absorbed by the leather or may react with collagen at one site only. Syntans include various polymers and copolymers, such as those obtained by condensing formaldehyde with, for example, phenols and/or aryl sulphonates, and acrylate, methacrylate, acrylamide and/or acrylonitrile homopolymers and copolymers. Formaldehyde itself and dialdehydes such as glutaraldehyde are also used in tanning, usually in combination with other tannages.

For centuries the production of leather was based on the vegetable tannages which produce the characteristic brown colour traditionally associated with leather. One of the first mineral tannages was alum, but currently the most widely used tanning agent is chrome, usually in the form of basic chromium sulphate, which produces a blue grey leather with high shrink temperatures. However mineral tannages in general, and chrome tannages in particular are under pressure on environmental grounds. Syntans are less environmentally harmful than mineral tanning agents. However, many syntans are derived from formaldehyde, which may be released during tanning. Formaldehyde and difunctional aldehydes present a health hazard and are unpleasant to handle.

Tetrakis (hydroxymethyl) phosphonium salts which will be referred to herein as "THP salts" have long been used as fire-retardants for textiles and have been applied to the keratinous (fur) side of skins for this purpose. The salts may be applied directly to the fabric or in the form of precondensates which are water soluble or sparingly water soluble copolymers of THP with organic nitrogen compounds such as urea or an amine and which are referred to herein as "THP condensates". THP salts have also been known as possible ingredients of tanning liquors for more than thirty six years. US. 2 992 879 referred to THP chloride (THPC) as an unsatisfactory tanning agent on its own, and recommended a combination of THPC and a phenol such as resorcinol speculating that the two react together to form an effective tanning agent when the pH is raised. In fact THP salts do copolymerise with phenols such as resorcinol (see, for example, Textile Research Journal, December 1982, P743). US 3 104 151 describes the use of such THPC phenol copolymers as light pretannages for leather in which the main tannage is vegetable or mineral. GB 2 287 953 describes the use of THP salts as cross linkers in conjunction with melamine formaldehyde or urea formaldehyde prepolymers, in order to form a copolymeric tanning agent in situ in the tanning liquor. EP 0 559 867 describes the use of phosphonium salts such as THP sulphate (THPS) on raw or cured skin prior to tanning e.g. in acid degreasing. EP 0 681 030 describes the use of THPS as a cross linker for casein finishes applied to leather after tanning. GB 2 314 342 describes the use of hydroxyalkyl phosphines and phosphonium salts as tanning agents in conjunction with aromatic anionic syntans and EP O 808 908 describes the use of THP salts with condensable nitrogen compounds.

THP salts are stable under acidic conditions in the absence of air or oxidising agents. At pH above 3 and in the absence of oxidising agents they are gradually converted to the parent base, tris(hydroxymethyl)phosphine herein referred to as THP. Conversion is rapid and substantially complete between pH of about 4 and 6. Above pH 7, or in the presence of oxidising agents THP salts or THP are converted to tris(hydroxymethyl)phosphine oxide (THPO), conversion being rapid and substantially complete at pH above about 10, e.g. 12. It has been stated, e.g. in US 2 993 744, that THPO is the effective tanning agent in THP based tannages.

Contrary to statements in the art, THPO is not effective as a tanning agent for leather, and THP salts are also ineffective as tannages. Moreover THP used in conjunction with co-condensable monomers or polymers provides complex systems which are difficult to control to obtain consistent results. However THP on its own is an effective main tanning agent. THP is usually most effective when formed in situ by first impregnating the leather with a THP salt, in the substantial absence of monomers or prepolymers which react or copolymerise with THP and raising the pH above 4 and preferably above 5.

In addition to THP, compounds of the formula $R P(CH_2OH)_2$, referred to herein as "THP analogues", where R is an organic group which does not react chemically with collagen, such as a C_{1-20} alkyl, alkenyl, aryl, aralkyl, alkaryl, polyalkyleneoxy, alkylpolyalkyleneoxy or polyalkyleneoxy alkyl group are highly effective tanning agents.

For convenience "THP" will be used herein, where the context permits, to refer generically to THP, THP salts, THP condensates and THP analogues.

The steps required to produce leather including the pickling and degreasing which usually precede tanning, remove most of the natural oils and fats from leather. These are normally at least partially replaced after tanning by fat liquoring, which entails contacting the leather with an aqueous emulsion of oils and fats which soften and lubricate the finished leather. It has been found that leather which has been tanned with THP does not readily absorb fat liquor. THP generally gives a tight leather. It would be useful to be able to obtain the advantages of THP, but prepare a less tight and more easily fat liquored leather.

A further problem is swelling of the skin, control of which usually requires the presence of salts such as chloride or sulphate.

One object of the present invention is to provide tannages which exhibit the advantages of THP but which are less tight and/or more readily fat liquored.

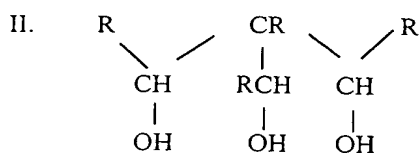
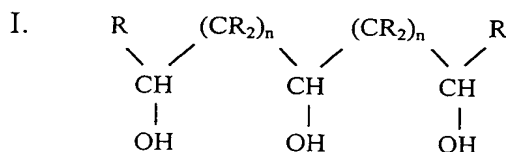
We have found that a mixture of THP with a water soluble compound containing at least three adjacent, geminal or vicinal >CH OH groups provides improved tanning compared with THP alone, and in particular provides a soft, less tight and more easily fat liquored product. The leather also shows reduced tendency to swelling which may be controlled without the use of salts.

We believe that THP interacts chemically with the polyhydroxy compounds possibly by hydrogen bonding.

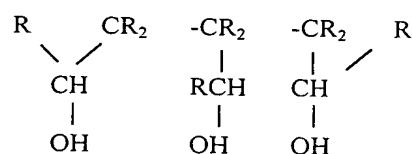
Our invention therefore provides a mixture of THP with a water soluble aliphatic polyhydroxy compound comprising at least three adjacent, geminal or vicinal >CH OH groups.

Our invention also provides a method of tanning or degreasing leather which comprises contacting collagen with a mixture as aforesaid.

The hydroxy methylene groups may be adjacent (i.e. directly linked as in glycerol), geminal (i.e. linked to the same carbon atom as in pentaerythritol) or vicinal (i.e. linked to adjacent carbon atoms, as in trimethylolpropane). Thus the polyhydroxy compounds useful in the invention comprise compounds of the formulae:



and III.



wherein each n may independently be 0, 1 or 2 and each R is independently hydrogen or an alkyl, a hydroxy- or polyhydroxy- alkyl, a carbonyl, a carboxyl, a C₁₋₂₅ acyl, a carbonyl- carboxy- or C₁₋₂₅ acyl- substituted alkyl group or an alkyl group or hydroxy-, carboxy- carbonyl- or C₁₋₂₅ acyl substituted alkyl group which is interrupted by one or more ether or carbonyl linkages or wherein two or more R groups may together constitute one or more alicyclic rings, optionally substituted with one or more hydroxy, carbonyl carboxy and/or acyl groups and/or interrupted by one or more ether or carbonyl linkages.

The aliphatic polyhydroxy compound may for example be glycerol, sorbitol, trimethylol propane, pentaerythritol, 1,2,3-trihydroxy butane, 1,2,3,4-tetrahydroxy butane,

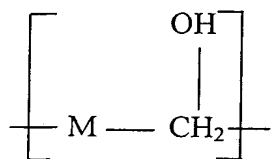
1,2,3-trihydroxy pentane, 2,3,4-trihydroxy pentane, tetrahydroxy pentane, pentahydroxy pentane, water soluble carbohydrates including mono and disaccharides and soluble starches and alginates. Examples of suitable carbohydrates include sucrose, glucose, maltose, lactose, dextrose, fructose, xylose, arabinose, mannose, ribose and rhamnose. The compound may also be a derivative of a carbohydrate including alkyl glycosides such as a C₁₋₂₅ alkyl glucoside or polyglucoside, or ascorbic acid, or alginates or C₁₋₂₅ acyl esters of either sucrose or sorbitan. Generally we prefer not to use nitrogen containing derivatives.

The relative proportion of THP and polyhydroxy compound may be equimolar or may comprise an excess of either component. Preferably the THP is in an excess of up to 20:1 molar, depending on the characteristics required. Generally the higher the proportion of polyhydroxy compound the less tight the leather. Proportions between 10:1 and 2:1 molar are generally preferred.

The THP and polyhydroxy compound may be premixed or mixed in situ in the tanning operation.

The THP may be used in conjunction with syntans, e.g. by treating the skin with said THP and a syntan (preferably a syntan which does not react with THP under normal tanning conditions) and/or by treating the skin in a plurality of stages at least one of which entails treatment with syntan and at least one other of which entails treatment with the THP.

For the purpose of this specification "syntan" is used to refer to replacement syntans which are synthetic organic compounds capable of reacting with collagen at two or more sites to form cross links and also to auxiliary syntans which do not in themselves contribute substantially to the cross linking but which are physically absorbed by the leather or react at no more than one site so as to modify the physical properties of the leather. For example the term includes any water soluble polymer prepared by copolymerising formaldehyde, which is capable of increasing the shrink resistance of collagen and which comprises at least two units of the formula



where each M is an aryl group such as a phenyl, naphthyl or aniline group substituted with one or more hydroxyl and/or sulphate, sulphone or sulphonimide groups or a urea or melamine residue. As used herein the term "syntan" also includes resin syntans which are homopolymers and copolymers of unsaturated carboxylic acids or their salts, esters, amides or nitriles, e.g. acrylic acid, methacrylic acid, acrylamide, acrylonitrile, maleic acid, fumaric acid, itaconic acid, aconitic acid, crotonic acid, isocrotonic acid, citraconic acid, mesaconic acid, angelic acid, tiglic acid and cinnamic acid. The copolymers may also comprise other vinylic comonomers such as styrene. Also included are acetone condensates with, for example sulphones and sulphonamides. Resin syntan may modify such properties as dye levelling, filling, grain appearance, break, grain strength, buffing nap, softness and tensile or tear strength.

The THP tends to react with nitrogen containing syntans and with other nitrogenous compounds and also to some extent with aromatic syntans. Such reactions may compete with cross linking reactions of both the THP and the syntan resulting in chaotic behaviour when the two are used together. Such systems are so highly sensitive to the conditions of use that it may be difficult or impossible to control them so as to obtain the consistent results required for a viable commercial process.

For these reasons we prefer not to use mixtures with such compounds. However it is possible to precondense the THP with, for example, cocondensable nitrogenous compounds such as urea, melamine, dicyandiamide and/or aliphatic amines to form condensates comprising two or more phosphorus atoms and having at least two hydroxymethyl groups.

High pH is preferably avoided because it converts the phosphine group to phosphine oxide, which is substantially ineffective as a tanning agent. We prefer that acetal solutions for use according to our invention should have a pH less than 10, more preferably less than 9, especially less than 8, typically less than 7.5, most preferably 4.5 to 7. We prefer that the THP contains less than 15%, more preferably less than 10%, e.g. less than 9% of THPO based on the weight thereof. Generally the less THPO present the better.

The THP is preferably used in a total concentration of from 0.01 to 20% by weight based on the total weight of the tanning liquor, more preferably 0.5 to 10%, e.g. 1 to 5%, most preferably 1.5 to 4%. The total proportion of the THP used is preferably from 0.3 to 20% by weight based on the weight of wet skin, more preferably 1 to 15%, especially 1.5 to 10%, most preferably 2 to 5%.

We particularly prefer processes in which skins are treated with an auxiliary syntan prior to tanning with the THP.

When the mixture is used in combination with a syntan, the latter is preferably a polyacrylate, polymethacrylate, or copolymer of acrylic and/or methacrylic acid with acrylonitrile and/or acrylamide. Typically the polymer has a molecular weight in the range 1,000 to 200,000, more usually 3,000 to 100,000.

The syntan is preferably present at a concentration of from 0.5 to 35% by weight of the tanning liquor. e.g. 1 to 20%, more preferably 2 to 10% especially 3 to 6%. The total proportion of syntan used is preferably from 1 to 20% by weight based on the wet weight of skins, e.g. 2 to 10% especially 3 to 5%.

The proportion by weight of THP to syntan may typically be from 1:10 to 10:1, preferably 1:5 to 2:1, especially 1:2 to 1:1. The total proportion of tannages used is preferably from 2 to 20% active weight based on the wet weight of skins, e.g. 3 to 10%, especially 4 to 8%. The total tannage used preferably comprises more than 80% by weight, more preferably more than 90% by weight, e.g. more than 95% of the THP and syntan. Where white leather is required, we prefer that the total tannages consist essentially of the THP and syntan. In particular we prefer the leather is not tanned with vegetable or mineral tannage.

The THP is preferably applied in the substantial absence of monomers or prepolymers capable of copolymerising with the THP such as phenol, urea, melamine or their precondensates with formaldehyde. For the purposes of this specification, "the substantial absence of monomers or prepolymers" means less than the minimum that would be capable of reacting or copolymerising with 50% of the THP, more preferably less than the minimum that would be required to react or copolymerise with 20%, e.g. less than 5% by weight based on the weight of THP, most preferably less than 2%, especially less than 1%.

The THP may be applied as a first tanning step with a syntan as a retan. Preferably the THP is applied to acidified skins following aqueous degreasing. E.g. the initial pH is typically below 5, e.g. below 4. We prefer that the pH be raised above 5 and preferably maintained above 6 for the main duration of the tanning process.

The skins are preferably agitated in the tanning liquor for a sufficient time to raise the shrink temperature above 75°C, more preferably above 80°C, most preferably above 85°C.

According to a particularly preferred embodiment the polyhydroxy compound is a surfactant such as a C₆₋₂₅ alkyl polyglycoside, sucrose ester or sorbitan ester and the THP and polyhydroxy compound are applied to undegreased or partially degreased skins, in order to effect degreasing or further degreasing thereof.

The tanned skins are typically washed with warm water and fat liquored using a suitable oil or blend of oils. Fat liquoring is normally carried out after dyeing.

The invention will be illustrated by the following examples.

Example 1

60g pickled bovine skin was rotated for 10 minutes with 15% based on the wet weight on skin of 8% sodium chloride solution. 3% based on the wet weight of skin of 75% by wt. THP solution and 1% sucrose was added and the mixture rotated for 3 hours. The solution was basified to pH 6.5 by adding 2.25% based on the wet weight of skin of sodium bicarbonate and the skins left to rotate overnight.

After the first 3 hours penetration was tested with sodium selenite solution. A pale, even colour indicated even penetration throughout the skin. In contrast a control using THPS without sugar gave only surface action.

After basification a further sample was tested with sodium selenite solution. A strong orange colouration evenly distributed was observed throughout the skin. THP alone gave an uneven colouration. The example was repeated three times using respectively maltose, lactose and D-glucose instead of sucrose, all with similar results.

All the samples gave similar shrink temperatures within the range 81-83°C except for the lactose which gave a shrink temperature of 78°C, but the THP control felt hard and boardy while the other samples were soft and pliable.

Example 2

400g of brine pickled pelt was rotated for 10 minutes with 15% by weight of water based on the wet weight of the skins at pH 4.6. 3% THP based on the wet weight of skins was added as a 75% aqueous solution together with 3%, based on the wet weight of skins, of glycerol. After 3 hours rotation at 35°C the pH was 3.38 and the shrink temperature was 58°C after basifying to pH 4.2 with sodium bicarbonate the shrink temperature was 64°C. Basification to pH 5.5 gave a shrink temperature of 68°C. Further basification to pH 6.5 gave a shrink temperature of 77°C.

Testing with sodium selenite showed even penetration and the product was soft and pliable.